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SYNTHESIS AND INSECTICIDAL PROPERTIES OF SOME ESTERS OF PHOSPHORIC ACIDS

N. N. Mel'nikov, Ya. A. Mandel'baum, P. V. Popov Submitted 11 January 1950 Fresented by Academician S. I. Vol'fkovich 12 January 1950

Esters of monothiophosphoric acid with the general formalas (RO)3PS, (00)2FSOC6H4NO2, and ROFS(OC6H4NO2)2 were synthesized and investigated for their insecticidal effectiveness against Aphis fabae Scop. and Calandra granaria L.

The majority of the esters were obtained with satisfactory yields, as can be seen in appended Tables 1 and 2. Table 3 gives the minimum amounts of each compound in powder form required to insure 100-percent extermination of the two pests.

The tables list dialkyl-nitrophenylthiophosphates, all of which are liquids and which can be distilled only in a high vacuum if decomposition is to be prevented. Monoalkyldinitrodiphenlthiophosphates, which are solid substances, have been also listed in the tables.

DDT (4,4'-dichlorodiphenyltrichloromethylmethane), GKhTsG (hexachlorocyclohexane), and anabasine are included in the final table for comparison with the phosphoric esters. The data presented in Table 3 permits the authors to make the following conclusions:

- Methyl- and ethylnitrophenylthiophosphates are the most active compounds.
- 2. An increase in the molecular weight of an alkyl radical in a mixed ester of monothiophosphoric acid results in a decrease in its insecticidal activity.

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- 3. The position of the nitro group in the phenyl radical of a mixed ester of menothiophosphoric acid is of great importance. Of the three isomers in the table, the greatest toxicity is exhibited by diethyl-4-nitrophenylthiophosphate and the least by diethyl-3-nitrophenylthiophosphate.
- 4. Dialkyl-nitrophenylthiophosphates are more active than monoalkyldinitrodiphenylthiophosphates and trialkylthiophosphates.
 - 5. Trinitrotriphenylphiophosphate is almost completely inactive.
- Several of the phosphoric esters are very active, and many of them are more active than DDT and GKhTsG.

In printing to the value of phosphoric acid esters both as (1) ordinary insect chas and (2) in the internal therapy of plants, attention is called in the first instance to page 18 of Theses of the 19th Plenum of the Section of Plant Care, by Mel'nikov and Popov, published by the All-Union Academy of Agricultural Sciences ineni Lenin, Stalinabad, 1949, and, in the second case, to an article by H. Coates in Ann. App. Biol, Vol XXXVI, page 156, 1949.

TABLE 1

Name, Formula		Boiling Point (in deg C)	Yield (in %)	
Methyl-4,4'-dinitrodiphenylthiophosphate CH ₃ OPS(OC ₆ H ₄ NO ₂) ₂ Ethyl-4,4'-dinitrodiphenylthiophosphate C ₂ F ₅ CP3(CC ₆ H ₄ NO ₂) ₂ Ethyl-3,2'-dinitrodiphenylob iophosphate C2H ₅ OPS(OC ₆ H ₄ NO ₂) ₂ Fichyl-4,4'-dinitrodiphenylthiophosphate C ₂ H ₇ OF3(OC ₆ H ₄ NO ₂) ₂ Inegropyl-4,4'-dinitrodiphenylthiophosphate ('H ₃) ₂ CHOPS(OC ₆ H ₄ NO ₂) ₂ Buytl-h,4'-dinitrodiphenylthiophosphate C+H ₃ OF3(OC ₆ H ₄ NO ₂) ₂		145-147	51	
		126-127	90	
		91-82	90	
		92-93	65	
		96-97	5.1	
		57-58	80	
4,5',4''-trinitrotriphenylthiophospha (Ω ₂ MC ₅ H ₄ O) ₃ P3	ate	175-176	50	
TABLE 2				
Menne, Formula	²⁰	n25	Yield (in %)	
Dimethyl-4-nitrophenylthiophosphate (CH30)2FSOC6H4NO2 Diethyl-2-nitrophenylthiophosphate (C2H O)2FSOC6H4NO2 Diethyl-3-nitrophenylthiophosphate (C2H50)2FSOC6H4NO2 Diethyl-4-nitrophenylthiophosphate (C2H50)2FSOC6H4NO2 Dipropyl-4-nitrophenylthiophosphate (C3H70)2FSOC6H4NO2 Disopropyl-4-nitrophenylthiophosphate (C3H70)2FSOC6H4NO2 Disopropyl-4-nitrophenylthiophosphate (CCH3)2CHC72FSOC6H4NO2 Dibutyl-4-nitrophenylthiophosphate (C4H90)2FSOC6H4NO2	1.3518	1.5600	80	
	1.2551	1.5255	50	
	1.2801	1.5262	79	
	1.2704	1.5374	80	
	1.2123	1.5327	65	
	1.2101	1.5378	60	
	1.1640	1.5311	27 :	
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TABLE 3

Min Amt (in %) of the Compound Contained in a Powder Prep Required to Produce 100% Extermination

Name_	Aphis fabae Scop.	Calandra granaria L.
Methyl-4,4'-dimitroc phenylthiophosphate	1.25-2.5	-
Ethyl-3,3'-dinitrodiphenylthiophosphate	-	5
Ethyl-4,4'-dinitrodiphenylthiophosphate	0.1-0.25	0.1-0.25
Propyl-4,4'-dinitrodiphenylthiophosphate	-	5 .
Isopropyl-4,4'-dinitrodiphenylthiophosphate	-	5
Buty1-4,4'-dinitrodiphenylthiophosphate	-	5
Dimethyl-4-nitrophenylthiophosphate	0.3-0.6	-
Diethyl-2-nitrophenylthiophosphate	0.15-0.3	_
Diethyl-3-nitrophenylthiophosphate	-	5
Diethyl-4-nitrophenylthiophosphate	0.012-0.025	0.012-0.025
Dipropyl-4-nitrophenylthiophosphate	-	5
Diisopropyl-4-nitrophenylthiophosphate	-	5
Dibutyl-4-nitrophenylthiophosphate	_	5
Trimethylthiophosphate	1.25-2.5	-
Triethylthiophosphate	1-2.5	0.5-1
4,4',4''-trinitrotriphenylthiophosphate	>10	>10
DDT	> 5.5	> 5,5
GKhTsG	3.5-7	3.5-7
Anabasine sulfate (on talcum)	1-2.5	5

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